PRODUCTION OF SILICONE RAW MATERIAL POWDER FOR SOLAR CELL AND SILICONE INGOT FOR SOLAR CELL

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Inventor(s): ARAYA MATAO; NISHIIKE UJIHIRO +
Applicant(s): KAWASAKI STEEL CO +
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Abstract of **JP 9165212 (A)**

PROBLEM TO BE SOLVED: To provide the methods for producing high purity silicone raw material powder and high purity silicone ingot usable for silicone for solar cell. SOLUTION: A solid prepared by removing liquids from silicone sludge generated in slicing process of a silicone ingot into a wafer is used as raw material. The silicone raw material powder is obtained by removing the impurities in the solid in a signal process or a combination of the processes, where the solid is immersed in an acid solution and a magnetic separation in a magnetic field especially >=1T or two step separation using a magnetic field <=1T and a magnetic field >=1T, etc., is carried out, and successively washing and drying. This silicone raw material powder or pellets produced by pressing the powder are put into a high purity molten silicone bath, or whole or a part of powder is blown in with Ar or H2 gas, melted and coagulated in one direction to give a high purity silicone ingot.

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(71)出願人　000001258
川崎製鉄株式会社
兵庫県神戸市中央区北本町通1丁目1番28号

(72)発明者　荒谷　復夫
千葉県千葉市中央区川崎町1番地　川崎製鉄株式会社技術研究所内

(72)発明者　西池　氏裕
東京都千代田区内幸町2丁目2番3号　川崎製鉄株式会社内

(74)代理人　弁理士　小林　英一

(54)【発明の名称】　太陽電池用シリコン原料粉および太陽電池用シリコンインゴットの製造方法

(57)【要約】

【課　題】　太陽電池用シリコンの原料となりうる高純度シリコン原料粉および高純度シリコンインゴットの製造方法を提案する。

【解決手段】　シリコンインゴットをスライスしてウェーハに加工する時に発生するシリコンスラッジを素材として、該素材から液体を除去したのちの固形分について、酸溶液に浸漬する工程、磁場中とくに１Ｔ以上の磁場中あるいは１Ｔ未満の磁場および１Ｔ以上の磁場中の２段階磁気分離を施す工程等を単独あるいは組み合わせることにより、固形分中の不純物を除去したのち、洗浄および乾燥してシリコン原料粉を得る。このシリコン原料粉あるいはこれら粉を押固めたペレットを高純度溶融シリコン浴中に投入あるいは原料粉の全部又は１部をArガスあるいはH_2ガスとともに吹込み、溶解して一方向凝固により高純度シリコンインゴットを得る。

【特許請求の範囲】

【請求項１】　シリコンインゴットをスライスしてシリコンウェーハに加工する際に発生するシリコンを主成分とするシリコンスラッジを素材として、該素材から固形分を分離したのち、該固形分を酸溶液に浸漬し不純物を除去する酸浸漬工程と、さらに洗浄および乾燥工程を経ることを特徴とする太陽電池用シリコン原料粉の製造方法。

【請求項２】　シリコンインゴットをスライスしてシリコンウェーハに加工する際に発生するシリコンを主成分とするシリコンスラッジを素材として、該素材から固形分を分離したのち、該固形分から物理的手段により不純物を除去する物理的分離工程と、ついで酸溶液に浸漬し不純物を除去する酸浸漬工程と、さらに洗浄および乾燥工程を経ることを特徴とする太陽電池用シリコン原料粉の製造方法。

【請求項３】　シリコンインゴットをスライスしてシリコンウェーハに加工する際に発生するシリコンを主成分とするシリコンスラッジを素材として、該素材から固形分を分離したのち、該固形分を１Ｔ以上の磁場中を通過させ不純物を分離する磁気分離工程を経て、さらに洗浄および乾燥工程を経ることを特徴とする太陽電池用シリコン原料粉の製造方法。

【請求項４】　シリコンインゴットをスライスしてシリコンウェーハに加工する際に発生するシリコンを主成分とするシリコンスラッジを素材として、該素材から固形分を分離したのち、該固形分を１Ｔ以上の磁場中を通過させ不純物を分離する磁気分離工程と、ついで酸溶液に浸漬し不純物を分離する酸浸漬工程と、さらに洗浄および乾燥工程を経ることを特徴とする太陽電池用シリコン原料粉の製造方法。

【請求項５】　前記磁気分離工程が、該固形分を１Ｔ未満の磁場あるいは１Ｔ以上の磁場中を通過させたのち、さらに１Ｔ以上の磁場中を通過させる２段階磁気分離工程であることを特徴とする請求項３又は４記載の太陽電池用シリコン原料粉の製造方法。

【請求項６】　前記１Ｔ以上の磁場の形成が超電導マグネットによることを特徴とする請求項３、４又は５記載の太陽電池用シリコン原料粉の製造方法。

【請求項７】　シリコンインゴットをスライスしてシリコンウェーハに加工する際に発生するシリコンスラッジを素材として得られたシリコン原料粉又は、該シリコン原料粉より得たシリコン原料ペレットを、溶融した高純度シリコン浴に投入し溶解する溶解工程と溶融シリコンを一方向凝固により凝固させる凝固工程によりインゴットとすることを特徴とする太陽電池用シリコンインゴットの製造方法。

【請求項８】　前記溶解工程が、該シリコン原料粉の全部又は１部を不活性ガス又は水素ガスとともに溶融高純度シリコン浴に吹込むことを特徴とする請求項７記載の太陽電池用シリコンインゴットの製造方法。

【請求項９】　前記シリコン原料粉が、請求項１、２、３、４、５又は６記載の製造方法で製造されたものである請求項７又は８記載の太陽電池用シリコンインゴットの製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、高純度シリコンの製造に関し、特に太陽電池用シリコンの原料として用いることができる高純度シリコンの製造方法に関する。

【０００２】

【従来の技術】近年、エネルギー源の多様化の要求から、太陽光発電が脚光を浴び、低価格発電装置の実用化に向け研究開発が盛んに行われている。このような状況の中で、太陽電池用原料としてシリコンは最も汎用されやすい材料であり、しかも、動力用電力供給に使われる材料として最も重要視されている。

【０００３】太陽電池の原料となりうるシリコンは、純度 99.9999%以上で、比抵抗 0.5～10Ωcm（シリコン中のＢ濃度に換算して0.2ppm以下）という高純度が要求されており、従来、半導体産業で用いられる高純度シリコン又はＩＣ用の基板を製造したときに発生する規格外品が利用されている。しかし、半導体用高純度シリコンは高価であり、また規格外品の発生量は少なく、量に限りがある。今後、太陽電池の増加が予想され、太陽電池用シリコン源の確保が重要な課題となっている。

【０００４】このようなことから、太陽電池用シリコンを安価にしかも安定して供給できる方法が検討され、多くの提案がなされている。例えば、市販のシリコン（純度99.5wt%）から上記高純度シリコンを製造する方法として、Al、Fe、Ti等の金属不純物元素については固液分配係数の小さいことを利用した一方向凝固精製により除去し、Ｃについては、SiC となっている場合には凝固の際に表面に析出させ、また溶解している場合にはCOとして除去し、一方、Ｐについては蒸気圧の高いことを利用して減圧除去し、Ｂについては H_2O、CO_2 あるいはO_2を添加したArプラズマ溶解により除去する方法が提案されている。

【０００５】しかし、上記製造方法では、各不純物元素の除去方法がそれぞれ異なり、工程が煩雑になるばかりか、次工程に移行する際のロスによる歩留りの低下等の問題があった。一方、最近、電子ビーム溶解により市販の金属シリコン中のＰ、Ca、Al、Ｃ、Ｂの同時除去が可能であることが報告され（ISIJ Intrernational, Vol.32(1992), No.5, P.635～P.642 ）、製造工程の簡略化が期待されている。しかし、これは、シリコン中のＢ濃度が10ppm 程度まで低減したという程度のものであり、太陽電池シリコンとして目標とされているＢ濃度以下に達してはいない。

【０００６】一方、特公平5-124809号公報には、電子ビ

ーム溶解を利用した一方向凝固精製により不純物を除去する方法が提案されているが、一方向凝固精製は蒸発による精製とは精製の機構が異なり、固液分配係数が１に近い不純物であるＢ等の効率的除去を行うのは困難であった。また、例えば特公平5-31488 号公報には、溶融金属シリコンに粉状の珪石を吹込み SiOガスを発生させ、該 SiOガスを還元剤が充填した層内で金属Siに還元することにより高純度シリコンを得ようとする方法が提案されている。

【０００７】さらに、特開平5-246706号公報には、冶金用シリコンを出発原料として溶融し、溶融シリコンと上部に設けた電極間にアークをとばすとともに、不活性ガス、好ましくは酸化性ガスを添加することにより精製し、高純度シリコンを得る方法が提案されている。しかしながら、シリコン中のＢやＰを除去することが難しく、工業的生産には移行できていないのが現状で、高純度シリコン基板を得るための高純度シリコン源を安価に、安定して確保できていないという問題が残されている。

【０００８】

【発明が解決しようとする課題】本発明は、上記課題を有利に解決し、太陽電池用高純度シリコンの原料となるシリコン原料粉あるいはペレットおよびこれら原料粉およびペレットを用いて太陽電池用高純度シリコンを得ることができるシリコンインゴットの製造方法を提案することを目的とする。

【０００９】

【課題を解決するための手段】本発明者らは、シリコン源として、従来廃却されていたシリコンスラッジに着目し、スラッジの利用方法について鋭意検討した結果、本発明を構成した。すなわち本発明は、シリコンインゴットをスライスしてシリコンウェーハに加工する際に発生するシリコンを主成分とするシリコンスラッジを素材として、該素材から固形分を分離したのち、該固形分を酸溶液に浸漬し不純物を除去する酸浸漬工程と、さらに洗浄および乾燥工程を経ることを特徴とする太陽電池用シリコン原料粉の製造方法であり、また、シリコンスラッジから固形分を分離したのち、該固形分から物理的手段により不純物を除去する物理的分離工程と、ついで酸浸漬工程と、さらに洗浄および乾燥工程を経る太陽電池用シリコン原料粉の製造方法である。また、本発明は、該固形分から不純物を除去する工程として、１Ｔ以上の磁場中を通過させる磁気分離工程を用いても、また、１Ｔ以上の磁場中を通過させる磁気分離工程と、ついで酸浸漬工程とを用いてもよい。また、本発明では、前記磁気分離工程が、該固形分を１Ｔ未満の磁場あるいは１Ｔ以上の磁場中を通過させたのち、さらに１Ｔ以上の磁場中を通過させる２段階磁気分離工程としてもよく、また、前記１Ｔ以上の磁場の形成は超電導マグネットを用いるのが望ましい。また、本発明は、上記した方法により製造されたシリコン原料粉又は、該シリコン原料粉をかためたシリコン原料ペレットを、溶融した高純度シリコン浴に投入し溶解する溶解工程と溶融シリコンを一方向凝固により凝固させる凝固工程によりインゴットとすることを特徴とする太陽電池用シリコンインゴットの製造方法である。また、本発明は、前記溶解工程が、該シリコン原料粉の全部又は１部を不活性ガス又は水素ガスとともに溶融高純度シリコン浴に吹込む溶解工程としてもよい。

【００１０】

【発明の実施の形態】本発明では、素材として、シリコンスラッジを用いる。シリコンスラッジは、シリコンインゴットをスライスしてシリコンウェーハに加工する際に発生するものである。このスライスに際し、切り代によって数十％のシリコンが切削くずとなる。このとき発生するスラッジは不純物が多くなるので、従来はすべて廃却されていた。このスラッジには、インゴットを切断する時に発生する高純度シリコン粉と切削時に切断機の刃等の摩耗により発生するアルミナ、コランダム、鉄酸化物、鉄水酸化物、シリカ、酸化バリウム、酸化マグネシウム、Cu、Ｃ等の不純物が物理的に混入し、スラリー状となっている。

【００１１】シリコンスラッジは、まずスラリー中に含まれる切削油を除去し、シリコン粉等の固形分を分離する。シリコンスラッジは、必要に応じ粉砕を行ってもよい。スラリーの粘度が低いときは、フィルタープレスあるいは遠心分離機にかけて分離するのが好ましい。スラリーの粘度が高い場合には、温水など切削油の溶媒となりうる液体をスラリーに加え、粘度を低下させてから上記と同様の分離を行うのが望ましい。また、切削油の除去が不十分の場合には、分離して得られた固形分を再度溶媒時に溶かしてスラリー状とし分離を繰り返すとよい。

【００１２】なお、シリコンインゴットの切削油は、上記分離作業を容易にすること、あるいは排液処理などの環境上の問題を少なくすることから、水溶性の切削油が望ましい。つぎに、固形分から不純物を分離する。分離方法の１つとして、本発明では、酸浸漬工程をとる。酸溶液を用い、酸溶液中に固形分を投入し不純物を除去する。この酸溶液による処理により金属不純物、とくにCu、Feが除去される。ここで用いられる酸は、塩酸水溶液あるいは塩酸と硝酸の混合水溶液が好適である。とくに、水溶液の濃度は５～20 vol％塩酸水溶液、５～20 vol％塩酸＋１～10vol％硝酸混合水溶液が好ましい。

【００１３】また、物理的手段を利用し、不純物を除去してもよい。物理的手段としては、特に限定しないが、本発明では、とくに粒子分級、浮選、磁気分離が好適である。これらを単独で適用しても、これらを組合せて適用してもよい。また、物理的手段と酸浸漬を組合せてもよい。粒子分級は、粒子をその比重あるいは重量によっ

て分離する方法で、本発明では、特に湿式で分離する方法、なかでも沈降法、遠心法が好適であり、清澄分離装置（クラリファイヤ）、沈殿濃縮装置（シックナー）あるいは遠心式の分離機が好適である。

【0014】これにより、不純物のうち、耐火物、切削工具からの粗粒不純物、炭素、銅、SiC が主に分離可能である。浮選は、水溶液中における吸着を利用して固体表面のぬれを制御し、気泡によって微粒子の分離を行う方法である。溶液のpHを制御したり、捕収剤を添加し、さらに抑制剤、活性剤を使用して分離する。これにより炭素、SiC が主に分離できる。

【0015】磁気分離は、粒子の磁性のちがいを利用して、不均一磁界内で分離しようとするものである。一般的に、分散質と分散媒が存在している場合、相対磁化M'

【0016】

【数1】

$$M^{-1}=\frac{9(\chi_p-\chi_f)}{(3+\chi_p)(3+\chi_f)}H$$

【0017】ここにχ_p ：分散質の体積磁化率

χ_f ：分散媒の体積磁化率

H ：磁界の強さ

で示されることはよく知られている。混合した粒子を磁化勾配のある空間におくと、相対磁化率と勾配に比例した磁気力が発生して、その力により分離できる。F∝M' ∇Hの大きさの磁気力が発生する。１段階の磁気分離でも、他の分離方法と併用すれば、高純度シリコン原料粉を得ることができる。しかし、弱磁性の物質では上式は、$M'=(\chi_p-\chi_f)H$で近似される。例えば、Al_2O_3 のχ_p は、水中では10^{-5} のオーダーしかなく、強磁性の物質Fe_2O_3 のχ_p （10^{-3} のオーダー）に比して二桁小さい。他の弱磁性物質χ_p は、10^{-5} オーダーでそれらの間の分離は不可能であった。

【0018】また、特に粒径の小さい粒子の場合、磁化力がブラウン運動に打ち勝つことができないため、分離がむずかしい。そこで、本発明では、１T未満の磁場あるいは１T以上の磁場を有する磁気分離を行い、強磁性の不純物を分離したのち、さらに１T以上の磁場を有する磁気分離を適用するのが好ましい。１段階の磁気分離では、Al_2O_3 等の弱磁性の物質が分離できないためである。

【0019】これにより、アルミナ、リン酸化物の分離が可能となる。さらに好ましくは、１T以上の磁場を有する磁気分離には、超電導マグネットを用いて磁場を形成する。超電導磁石の励磁中に形成された強磁場内に被分離流体を流し、電磁力により微少粒子をフィラメントに付着せしめ、弱磁性粒子の分離を可能にする。

【0020】上記工程により、固形分中の不純物を除去したのち、さらに水で洗浄し乾燥する乾燥工程を経て、

シリコン原料粉とする。乾燥したのちのシリコン原料粉は、通常50μm以下（-320メッシュ）の微粉である。このシリコン原料粉は、99.99%以上の純度を有している。シリコン原料粉は、粉体のままでもよいが、造粒しペレット状にしたシリコン原料ペレットとしてもよい。

【0021】図１はシリコン原料粉の製造プロセスの１例を示す工程図である。このようにして製造したシリコン原料粉あるいはシリコン原料ペレットを、予め溶融した高純度シリコン浴に投入し、溶解して一方向性凝固させインゴットを製造する。溶解はArなどの不活性雰囲気下でシリカルツボ中で行うのが好ましい。

【0022】シリコン原料粉をシリコン浴に投入する際には、不活性ガス雰囲気中で行ってもよいが、Ar又はH_2とともに、その全部又は一部をシリコン浴中に吹込むと、原料粉表面の酸化膜の酸素によりシリコン中の炭素を除去することができる。溶融したシリコン中には、除去が不十分な不純物や、溶融過程で耐火物などから混入する不純物が含まれるため、溶融後のシリコンを一方向凝固法により凝固させ、不純物を最終凝固部に集めて、これを凝固後に切断除去する。このときの一方向凝固での凝固速度は5mm/min以下、望ましくは2mm/min以下が適当である。

【0023】また、溶融シリコンの純度が低いときは、さらに、例えばBの低減には、H_2O、CO_2 、O_2を添加したArプラズマ溶解により除去することができる。その場合には、プラズマガス中に 10vol%以下のH_2O 、CO_2 、O_2を添加するのが好適である。図２に、シリコンインゴットの製造プロセスを示す。

【0024】

【実施例】

〔実施例１〕半導体用の単結晶基板をスライスしたときのシリコンスラッジを温水中で解砕後、遠心分離して切削油を分離し表１に示すシリコンスラッジ（固形分）を得た。上記固形分５kgを、HCl 10vol %＋HNO_3 5 vol%を含む混酸水溶液５ｌに浸漬したのち、水洗し、乾燥し、シリコン原料粉 4.5kgを得た。このシリコン原料粉の不純物の濃度を表１に示す。

【0025】つぎに、該シリコン原料粉 4.5kgを、Ar雰囲気中で1500℃に加熱されたシリカルツボ中で溶解した半導体用の高純度シリコン（３kg）の浴表面上に投入し、溶解した。得られた溶融シリコンは、 7.2kgであり、これをシリカでコーティングした黒鉛鋳型に鋳込み、上部から加熱し、下部より冷却することで１mm/minの速度で一方向凝固させた。凝固後、インゴットの上部15%を切断除去して 6.1kgのシリコンを得た。得られたシリコンインゴットの純度は表１に示す。太陽電池用シリコンとして十分の純度であり、シリコンスラッジ（固形分）の約70%が太陽電池用シリコンとして利用できたことになる。

【0026】スラッジから液を分離し、乾燥しただけの

固形分を、高純度シリコン浴に投入し溶解し、一方向凝固させてインゴットとしたものを比較例とした。比較例は、C、Fe、Cu等の不純物が多い。

【0027】

【表1】

シリコン原料粉およびシリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
スラッジ固形分（液分離後）	1	0.5	3500	1800	4500	素材
シリコン原料粉	0.4	0.1	500	300	4000	実施例
シリコンインゴット	0.3	<0.1	10	15	45＊	実施例
シリコンインゴット	0.5	0.3	100	35	80＊	比較例

＊：インゴット中心部の値

【0028】〔実施例2〕実施例1と同様にして得たシリコン原料粉 5.0kgを、Ar雰囲気中で1500℃に加熱したシリカルツボで溶解した半導体用高純度シリカ（3kg）の浴面上に投入し溶解したのち、さらにシリコン原料粉500gをシリカチューブを用いてArガスとともに溶融シリコン中に吹込んだ。このとき、ガス吹込みによりスプラッシュが発生したため、得られた溶融シリコンは 7.1kgであった。これをシリカでコーティングした黒鉛鋳型に鋳込み上部から加熱し、下部より冷却することにより1mm/minの速度で一方向凝固させた。凝固後、インゴットの上部15%を切断除去して6kgのシリコンインゴットを得た。得られたシリコンインゴット不純物分析値を表2に示す。最終的に得られたシリコンインゴット中の炭素含有量は5ppm 以下となった。太陽電池用シリコンとして十分な純度となっている。最終的に得られたシリコンの量は、シリコン原料粉の60%に相当する。

【0029】

【表2】

シリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
シリコンインゴット	0.15	<0.1	10	15	<5.0	実施例

【0030】〔実施例3〕半導体用の単結晶基板をスライスしたときのシリコンスラッジを温水に浸漬し、遠心分離機により液体を分離し、表1に示す純度と同じ純度のシリコンスラッジ（固形分）を得た。上記シリコンスラッジ（固形分）を、 0.8Tの磁界中で磁気分離を施したのち、さらに3Tの超電導マグネットにより発生させた磁界中で第2段の磁気分離を施したのち、水洗、乾燥し、シリコン原料粉を得た。このシリコン原料粉の不純物分析値を表3に示す。

【0031】つぎに、得られたシリコン原料粉を用いて、シリコンインゴットを製造した。シリコン原料粉5kgをシリカルツボで溶解した半導体用高純度シリコン（3kg）の浴面上に投入し溶解した。得られた溶融シリコンをシリカでコーティングした黒鉛鋳型に鋳込み、2mm/minの速度で一方向凝固させた。凝固後、インゴット上部を切断除去した。

【0032】得られたインゴットの不純物分析値を表3に示す。不純物は十分に除去低減されて、太陽電池用シリコンとして十分な純度になっている。

【0033】

【表3】

シリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
シリコン原料粉	0.3	0.2	100	50	15	実施例
シリコンインゴット	0.2	<0.1	< 1	<5	<5	実施例

【0034】〔実施例4〕半導体用の単結晶基板をスライスしたときのシリコンスラッジを温水に浸漬し、遠心分離機により液体を分離し、表1に示す純度と同じ純度のシリコンスラッジ（固形分）を得た。上記固形分を、 1.5Tの磁界中で磁気分離を施したのち、さらに3Tの超電導マグネットにより発生させた磁界中で第2段の磁気分離を施したのち、20%塩酸水溶液中に浸漬し、不純物を除去した。その後、酸溶液を除去したのち、水洗、乾燥し、シリコン原料粉を得た。このシリコン原料粉の不純物分析値を表4に示す。

【0035】つぎに、得られたシリコン原料粉を用いて、シリコンインゴットを製造した。シリコン原料粉5

kgをシリカルツボで溶解した半導体用高純度シリコン（3kg）の浴面上に投入し溶解した。得られた溶融シリコンをシリカでコーティングした黒鉛鋳型に鋳込み、2mm/minの速度で一方向凝固させた。凝固後、インゴット上部を切断除去した。

【0036】得られたインゴットの不純物分析値を表4に示す。不純物は十分に除去低減されて、太陽電池用シリコンとして十分な純度になっている。

【0037】

【表4】

シリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
シリコン原料粉	0.2	0.1	30	15	<5	実施例
シリコンインゴット	0.2	<0.1	<1	<5	<5	実施例

【0038】〔実施例5〕半導体用の単結晶基板をスライスしたときのシリコンスラッジを温水に浸漬したのち、遠心分離機によりシリコンスラッジ（固形分）とした。該固形分を 1.5Tの磁界中で磁気分離を施したのち、さらに20%HCl 水溶液中に浸漬し不純物を除去した。その後、酸溶液を除去したのち、水洗、乾燥し、シリコン原料粉を得た。このシリコン原料粉の不純物分析値を表5に示す。

【0039】つぎに、得られたシリコン原料粉を用いてシリコンインゴットを製造した。シリコン原料粉をシリカルツボで溶解した半導体用高純度シリコンの浴面上に投入し溶解した。溶融シリコンをシリカでコーティングした黒鉛鋳型に鋳込み、1mm/minの速度で一方向凝固させた。凝固後、インゴット上部を切断除去した。得られたインゴットの不純物分析値を表5に示す。

【0040】

【表5】

シリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
シリコン原料粉	0.3	0.3	250	100	20	実施例
シリコンインゴット	0.2	0.1	< 1	< 5	<5	実施例

【0041】

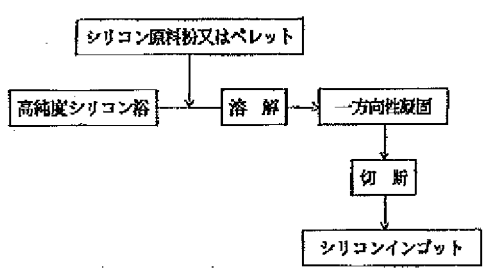
【発明の効果】本発明により、従来捨てられていた半導体シリコンのスラッジが太陽電池用素材として使用でき、太陽電池に必要な原料を安定して確保できるようになる。

【図面の簡単な説明】

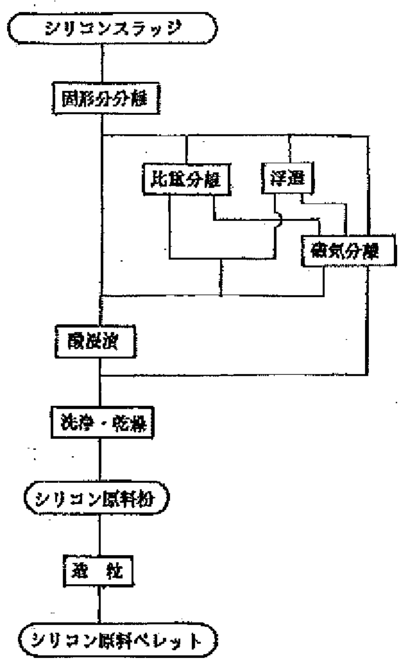
【図1】本発明のシリコン原料粉を製造するプロセスの一例を示す工程図である。

【図2】本発明のシリコンインゴットを製造するプロセスの一例を示す工程図である。

【図2】



【図1】



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CLAIMS

[Claim(s)]

[Claim 1]Are made from silicon sludge which uses as the main ingredients silicon by which it is generated when slicing a silicon ingot and processing it into a silicon wafer, A manufacturing method of an acid-dipping process of this solid content being immersed in an acid solution, and removing an impurity after separating solid content from this raw material, and silicon precursor powder for solar cells passing through washing and a drying process further.

[Claim 2]Are made from silicon sludge which uses as the main ingredients silicon by which it is generated when slicing a silicon ingot and processing it into a silicon wafer, A physical separation process of removing an impurity from this solid content by a physical means after separating solid content from this raw material, an acid-dipping process of it being immersed subsequently to an acid solution and removing an impurity, and a manufacturing method of silicon precursor powder for solar cells passing through washing and a drying process further.

[Claim 3]Are made from silicon sludge which uses as the main ingredients silicon by which it is generated when slicing a silicon ingot and processing it into a silicon wafer, A manufacturing method of silicon precursor powder for solar cells passing through washing and a drying process further through a magnetic-separation process of passing inside of a magnetic field beyond 1T for this solid content, and separating an impurity after separating solid content from this raw material.

[Claim 4]Are made from silicon sludge which uses as the main ingredients silicon by which it is generated when slicing a silicon ingot and processing it into a silicon wafer, A manufacturing method of a magnetic-separation process of passing inside of a magnetic field beyond 1T for this solid content, and separating an impurity after separating solid content from this raw material, an acid-dipping process of it being immersed subsequently to an acid solution and separating an impurity, and silicon precursor powder for solar cells passing through washing and a drying process further.

[Claim 5]A manufacturing method of the silicon precursor powder for solar cells according to claim 3 or 4, wherein said magnetic-separation process is a two-step magnetic-separation process of passing inside of a magnetic field beyond 1T after passing inside of a magnetic field below 1T, or a magnetic field beyond 1T for this solid content and also.

[Claim 6]A manufacturing method of the silicon precursor powder for solar cells according to claim 3, 4, or 5, wherein formation of a magnetic field more than said 1T is based on a superconductivity magnet.
[Claim 7]Silicon precursor powder obtained considering silicon sludge generated when slicing a silicon ingot and processing it into a silicon wafer as a raw material. Or a manufacturing method of a silicon ingot for solar cells considering it as an ingot according to a melting process which supplies a silicon material pellet obtained from this silicon precursor powder to a fused high-purity-silicon bath, and is dissolved, and a coagulating process which solidifies melted silicon by unidirectional solidification.
[Claim 8]A manufacturing method of the silicon ingot for solar cells according to claim 7, wherein said melting process blows all of this silicon precursor powder, or one copy into a melting high-purity-silicon bath with inactive gas or hydrogen gas.
[Claim 9]A manufacturing method of the silicon ingot for solar cells according to claim 7 or 8 with which said silicon precursor powder is manufactured by the manufacturing method according to claim 1, 2, 3, 4, 5, or 6.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]Especially this invention relates to the manufacturing method of the high purity silicon which can be used as a raw material of the silicon for solar cells about manufacture of high purity silicon.
[0002]
[Description of the Prior Art]In recent years, from the demand of diversification of an energy source, photovoltaics is brought into the limelight and research and development are briskly done towards utilization of a low-price power plant. In such a situation, as a raw material for solar cells, silicon is a material which is the easiest to be used widely, and, moreover, importance is most attached to it as a material used for the electric power supply for power.
[0003]The silicon which can serve as a raw material of a solar cell is purity. It is not less than 99.9999%, and is specific resistance. A high grade called 0.5-10-ohmcm (it converts into B concentration in silicon, and is 0.2 ppm or less) is demanded.
The substandard article by which it is generated when the high purity silicon used by semiconductor industry or the substrate for IC is manufactured conventionally is used.
However, the high purity silicon for semiconductors is expensive, and there are few yields of a substandard article, and quantity has a limitation. From now on, the increase in a solar cell is expected and reservation of the silicon source for solar cells has been important SUBJECT.
[0004]Since it is such, the method which is moreover stabilized and can supply the silicon for solar cells cheaply is examined, and many proposals are made. For example, as a method of manufacturing the above-mentioned high purity silicon from commercial silicon (purity 99.5wt%), About metallic impurity elements, such as aluminum, Fe, and Ti, unidirectional solidification refining using a solid-liquid distribution coefficient being small removes, and about C. When it is SiC, deposit the surface in the case of coagulation, and when dissolving, it removes as CO, On the other hand about P, decompression removal is carried out using steam pressure being high, and the method of removing by Ar plasma dissolution which added H_2O, CO_2, or O_2 is proposed about B.

[0005]However, in the above-mentioned manufacturing method, the removing methods of each impurity element differed, respectively, and there were problems, such as a fall of the yield by the loss at the time of a process shifting not only to becoming complicated but to a next process. On the other hand, P in the metal silicon of marketing by these days and electron beam melting, Ca, It is reported that simultaneous removal of aluminum, C, and B is possible (ISIJ Intrernational, Vol.32 (1992), No.5, P.635 to P.642), and simplification of the manufacturing process is expected. However, this is a thing of the grade that B concentration in silicon decreased to about 10 ppm.
Below B concentration made into the target as solar cell silicon is not reached.

[0006]On the other hand, although the way unidirectional solidification refining using electron beam melting removes an impurity is proposed by JP,H5-124809,B, Unidirectional solidification refining was difficult for the mechanisms of refining performing efficient removal of B etc. which are impurities with the solid-liquid distribution coefficient near 1 unlike refining by evaporation. For example, blow powdered silica into molten-metal silicon, JP,5-31488,B is made to generate SiO gas, and the method of making high purity silicon profitably like is proposed by returning to metal Si within the layer with which the reducing agent filled up ** SiO gas.
[0007]The silicon for metallurgy is fused as a starting material, while flying an arc to inter-electrode [which was provided in melted silicon and the upper part], to JP,H5-246706,A, it refines inactive gas and by adding a oxidizing gas preferably, and the method of obtaining high purity silicon is proposed. However, it is difficult to remove B and P in silicon, the actual condition is have not shifted to industrial production, and the problem that it is stabilized cheaply and the source of high purity silicon for obtaining a high-purity-silicon board cannot be secured is left behind.
[0008]
[Problem(s) to be Solved by the Invention]This invention solves an aforementioned problem advantageously and an object of this invention is to propose the manufacturing method of the silicon ingot which can obtain the high purity silicon for solar cells using the silicon precursor powder used as the raw material of the high purity silicon for solar cells or a pellet, these precursor powder, and a pellet.
[0009]
[Means for Solving the Problem]This invention persons constituted this invention, as a result of examining a utilizing method of sludge wholeheartedly as a silicon source paying attention to silicon sludge discarded conventionally. Namely, this invention is made from silicon sludge which uses as the main ingredients silicon by which it is generated when slicing a silicon ingot and processing it into a silicon wafer, An acid-dipping process of this solid content being immersed in an acid solution, and removing an impurity after separating solid content from this raw material, A physical separation process of being a manufacturing method of silicon precursor powder for solar cells passing through washing and a drying process furthermore, and removing an impurity from this solid content by a physical means after separating solid content from silicon sludge, Subsequently, they are an acid-dipping process and a manufacturing method of silicon precursor powder for solar cells which passes through washing and a drying process further. Even if a magnetic-separation process which passes inside of a magnetic field

beyond 1T is used for this invention as a process of removing an impurity from this solid content, subsequently an acid-dipping process may be used for it with a magnetic-separation process which passes inside of a magnetic field beyond 1T. It is good also as a two-step magnetic-separation process that said magnetic-separation process passes inside of a magnetic field beyond 1T in this invention after passing inside of a magnetic field below 1T, or a magnetic field beyond 1T for this solid content, and, as for formation of a magnetic field more than said 1T, it is desirable to use a superconductivity magnet. Silicon precursor powder manufactured by a method which this invention described above. Or it is a manufacturing method of a silicon ingot for solar cells considering it as an ingot according to a melting process which supplies a silicon material pellet which hardened this silicon precursor powder to a fused high-purity-silicon bath, and is dissolved, and a coagulating process which solidifies melted silicon by unidirectional solidification. Said melting process of this invention is good also as a melting process which blows all of this silicon precursor powder, or one copy into a melting high-purity-silicon bath with inactive gas or hydrogen gas.

[0010]

[Embodiment of the Invention]In this invention, silicon sludge is used as a raw material. Silicon sludge is generated, when slicing a silicon ingot and processing it into a silicon wafer. On the occasion of this slice, tens of% of silicon serves as cutting waste by end cost. Since impurities increased in number, the sludge generated at this time was discarded conventionally [all]. The high-purity-silicon powder by which it is generated in it when cutting an ingot in this sludge, and the alumina by which it is generated by wear of the edge of a cutting machine, etc. at the time of cutting, Impurities, such as corundum, iron oxide, iron hydroxide, silica, barium oxide, magnesium oxide, Cu, and C, mix physically, and serve as slurry form.

[0011]Silicon sludge removes the cutting oil first contained in a slurry, and separates solid content, such as silicon powder. Silicon sludge may grind if needed. When the viscosity of a slurry is low, it is preferred to apply and separate into the filter press or a centrifuge. When the viscosity of a slurry is high, since the fluid which can serve as a solvent of cutting oil, such as warm water, is added to a slurry and viscosity is reduced, it is desirable to perform the same separation as the above. When removal of cutting oil is insufficient, it is good to melt again the solid content produced by dissociating at the time of a solvent, to consider it as slurry form, and to repeat separation.

[0012]The cutting oil of a silicon ingot has the desirable cutting oil of water solubility [lessen / environmental problems, such as making the above-mentioned separation work easy or effluent processing,]. Next, an impurity is separated from solid content. As one of the separation methods, an acid-dipping process is taken by this invention. Using an acid solution, solid content is supplied in an acid solution and an impurity is removed. A metal impurity especially Cu, and Fe are removed by processing by this acid solution. A hydrochloric acid aqueous solution or the mixed water solution of chloride and nitric acid is preferred for the acid used here. Especially the concentration of solution has a 5-20 vol% hydrochloric acid aqueous solution and a preferred 5-20 vol% chloride+1-10vol% nitric acid mixed water solution.

[0013]A physical means may be used and an impurity may be removed. Especially as a physical means, although not limited, in especially this invention, particle classification, flotation, and magnetic separation

are preferred. These may be applied independently or it may apply combining these. A physical means and acid dipping may be combined. It is the way the specific gravity or weight separates particles, a sedimentation method and a centrifuge method are preferred for a particle classification also in the method of separating by a wet type especially in this invention, and a clear decollator (clarifier) and precipitate concentration device (thickener) or the separator of a centrifugal type is preferred for it.

[0014]Thereby, refractories, the coarse-grain impurity from a cutting tool, carbon, copper, and SiC are mainly disengageable among impurities. Flotation is the way control the wetting of a solid surface using the adsorption in solution, and air bubbles separate particles. The pH of a solution is controlled, or a collector is added and it dissociates further using a depressant and an active agent. Thereby, carbon and SiC can mainly dissociate.

[0015]It is going to separate magnetic separation within an uneven magnetic field using the difference of the magnetism of particles. Generally, when a dispersoid and carrier fluid exist, it is relative magnetization M^*. [0016]

[Equation 1]

$$M^{-1}=\frac{9\ (\chi_p-\chi_f)}{(3+\chi_p)\ \ (3+\chi_f)}H$$

[0017]here -- chi_p: -- bulk susceptibility chi_f: of a dispersoid -- bulk susceptibility H of carrier fluid : What is shown by magnetic field strength is known well. Also in space with magnetization inclination, the magnetic force proportional to relative magnetic susceptibility and inclination generates the mixed particles, and the power can separate. The magnetic force of the size of $F^{**}M^{*}{}^{**}H$ occurs. If even one step of magnetic separations are used together with other separation methods, high-purity-silicon precursor powder can be obtained. However, by the substance of feeble magnetism, an upper type is approximated by $M^*=(chi_p - chi_f)$ H. For example, underwater chi_p of Al_2O_3 has only an order of 10^{-5}, and is small double figures as compared with chi_p (order of 10^{-3}) of ferromagnetic substance Fe_2O_3. The separation between them was impossible for other feeble magnetism substance chi_p to the 10^{-5} order.

[0018]Since magnetizing force cannot overcome Brownian motion in the case of particles especially with small particle diameter, separation is difficult. Then, after performing magnetic separation which have a magnetic field below 1T, or a magnetic field beyond 1T in this invention and separating a ferromagnetic impurity, it is preferred to apply magnetic separation which have a magnetic field beyond 1T. In one step of magnetic separations, it is because a substance of feeble magnetism, such as Al_2O_3, is inseparable.

[0019]This becomes separable [alumina and a phosphorylation thing]. A magnetic field is formed in magnetic separation which have a magnetic field beyond 1T still more preferably using a superconductivity magnet. Pour a fluid to be dissociated in a strong magnetic field formed during magnetization of a super-conductive magnet, very small particles are made to adhere to a filament according to electromagnetic force, and separation of feeble magnetism particles is enabled.

[0020]By the above-mentioned process, after removing an impurity in solid content, it is considered as

silicon precursor powder through a drying process which is washed further with water and dried. Silicon precursor powder after drying is usually fines of 50 micrometers or less (-320 meshes). This silicon precursor powder has not less than 99.99% of purity. Although a granular material may still be sufficient as silicon precursor powder, it is good also as a silicon material pellet which was corned and was made into a pellet type.

[0021]Drawing 1 is process drawing showing one example of a manufacturing process of silicon precursor powder. Thus, manufactured silicon precursor powder or a silicon material pellet is supplied to a high-purity-silicon bath fused beforehand, unidirectional solidification is dissolved and carried out to it, and an ingot is manufactured. As for the dissolution, it is preferred under inert atmospheres, such as Ar, to carry out in a silica crucible.

[0022]although it may carry out in an inert gas atmosphere when throwing silicon precursor powder into a silicon bath -- Ar or H_2 -- the -- if a part is all blown during a silicon bath, carbon in silicon is removable by oxygen of an oxide film on the surface of precursor powder. Since an impurity with insufficient removal and an impurity mixed from refractories etc. in a melting process are contained in fused silicon, silicon after melting is solidified with an unidirectional solidification process, an impurity is brought together in a last solidified part, and cutting removal is carried out after solidifying this. Two or less mm/min is desirably suitable for coagulation speed in unidirectional solidification at this time 5 or less mm/min.

[0023]When purity of melted silicon is low, for reduction of B, Ar plasma dissolution which added H_2O, CO_2, and O_2 can remove further, for example. To in that case, inside of plasma gas It is preferred to add H_2O not more than 10vol%, CO_2, and O_2. A manufacturing process of a silicon ingot is shown in drawing 2.

[0024]

[Example]

[Working example 1] The silicon sludge (solid content) which centrifuges silicon sludge when the monocrystal substrate for semiconductors is sliced after a crack in warm water, separates cutting oil, and is shown in Table 1 was obtained. After 5 kg of the above-mentioned solid content is immersed in the mixed acid aqueous solution 5l containing HCl 10vol %+$HNO_3$5 vol%, it is rinsed, and it dries, and is silicon precursor powder. 4.5 kg was obtained. The concentration of the impurity of this silicon precursor powder is shown in Table 1.

[0025]Next, it is this silicon precursor powder. 4.5 kg was supplied on the bath surface of the high purity silicon (3 kg) for semiconductors which dissolved in the silica crucible heated by 1500 ** in Ar atmosphere, and it dissolved. They are the obtained melted silicon and 7.2 kg.
It cast to the graphite mold which coated this with silica, and heated from the upper part, and unidirectional solidification was carried out at the rate of 1 mm/min by cooling from the lower part.
After coagulation, cutting removal of 15% of the upper part of an ingot was carried out, and 6.1kg silicon was obtained. The purity of the obtained silicon ingot is shown in Table 1. It is purity sufficient as silicon for solar cells, and about 70% of silicon sludge (solid content) is able to use as silicon for solar cells.

[0026]What supplied to the high-purity-silicon bath, dissolved, separates liquid from sludge and used

[unidirectional solidification only of the dry solid content was carried out, and] it as the ingot was made into the comparative example. A comparative example has many impurities, such as C, Fe, and Cu.
[0027]
[Table 1]
シリコン原料粉およびシリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
スラッジ固形分（液分離後）	1	0.5	3500	1800	4500	素材
シリコン原料粉	0.4	0.1	500	300	4000	実施例
シリコンインゴット	0.3	<0.1	10	15	45 *	実施例
シリコンインゴット	0.5	0.3	100	35	80 *	比較例

*：インゴット中心部の値

[0028][Working example 2] Silicon precursor powder obtained like working example 1 After supplying 5.0 kg on the bath surface of the high purity silica (3 kg) for semiconductors dissolved by the silica crucible heated at 1500 ** in Ar atmosphere and dissolving, Furthermore, the silicon precursor powder 500g was blown into melted silicon with Ar gas using the silica tube. Melted silicon obtained since the splash occurred by gas blowing in at this time It was 7.1 kg. It cast to the graphite mold which coated this with silica, and heated from the upper part, and unidirectional solidification was carried out at the rate of 1 mm/min by cooling from the lower part. After coagulation, cutting removal of 15% of the upper part of an ingot was carried out, and a 6-kg silicon ingot was obtained. The obtained silicon ingot impurity analysis value is shown in Table 2. The carbon content in the silicon ingot obtained eventually was set to 5 ppm or less. It has purity sufficient as silicon for solar cells. The quantity of the silicon obtained eventually is equivalent to 60% of silicon precursor powder.
[0029]
[Table 2]
シリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
シリコンインゴット	0.15	<0.1	10	15	<5.0	実施例

[0030][Working example 3] Silicon sludge when the monocrystal substrate for semiconductors was sliced was immersed in warm water, the centrifuge separated the fluid, and the silicon sludge (solid content) of the same purity as the purity shown in Table 1 was obtained. After giving the magnetic separation of the 2nd step in the magnetic field which generated the above-mentioned silicon sludge (solid content) with the superconductivity magnet of 3T after giving magnetic separation in the magnetic field of 0.8T, it rinsed and dried and silicon precursor powder was obtained. The impurity analysis value of this silicon precursor powder is shown in Table 3.
[0031]Next, the silicon ingot was manufactured using the obtained silicon precursor powder. 5 kg of silicon precursor powder was thrown in on the bath surface of the high purity silicon (3 kg) for

semiconductors which dissolved by the silica crucible, and it dissolved. The obtained melted silicon was cast to the graphite mold coated with silica, and unidirectional solidification was carried out at the rate of 2 mm/min. Cutting removal of the ingot upper part was carried out after coagulation.

[0032]The impurity analysis value of the obtained ingot is shown in Table 3. Removal reduction is fully carried out and the impurity has purity sufficient as silicon for solar cells.

[0033]

[Table 3]

シリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
シリコン原料粉	0.3	0.2	100	50	15	実施例
シリコンインゴット	0.2	<0.1	< 1	<5	<5	実施例

[0034][Working example 4] Silicon sludge when the monocrystal substrate for semiconductors was sliced was immersed in warm water, the centrifuge separated the fluid, and the silicon sludge (solid content) of the same purity as the purity shown in Table 1 was obtained. After giving the magnetic separation of the 2nd step in the magnetic field which generated the above-mentioned solid content with the superconductivity magnet of 3T after giving magnetic separation in the magnetic field of 1.5T, it was immersed into a 20% hydrochloric acid aqueous solution, and the impurity was removed. Then, after removing an acid solution, it rinsed and dried and silicon precursor powder was obtained. The impurity analysis value of this silicon precursor powder is shown in Table 4.

[0035]Next, the silicon ingot was manufactured using the obtained silicon precursor powder. 5 kg of silicon precursor powder was thrown in on the bath surface of the high purity silicon (3 kg) for semiconductors which dissolved by the silica crucible, and it dissolved. The obtained melted silicon was cast to the graphite mold coated with silica, and unidirectional solidification was carried out at the rate of 2 mm/min. Cutting removal of the ingot upper part was carried out after coagulation.

[0036]The impurity analysis value of the obtained ingot is shown in Table 4. Removal reduction is fully carried out and the impurity has purity sufficient as silicon for solar cells.

[0037]

[Table 4]

シリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
シリコン原料粉	0.2	0.1	30	15	<5	実施例
シリコンインゴット	0.2	<0.1	<1	<5	<5	実施例

[0038][Working example 5] After silicon sludge when the monocrystal substrate for semiconductors was sliced was immersed in warm water, it was considered as silicon sludge (solid content) with the centrifuge. This solid content was immersed into 20 more%HCl solution, after giving magnetic separation in the magnetic field of 1.5T, and the impurity was removed. Then, after removing an acid solution, it

rinsed and dried and silicon precursor powder was obtained. The impurity analysis value of this silicon precursor powder is shown in Table 5.

[0039]Next, the silicon ingot was manufactured using the obtained silicon precursor powder. Silicon precursor powder was thrown in on the bath surface of the high purity silicon for semiconductors which dissolved by the silica crucible, and it dissolved. Melted silicon was cast to the graphite mold coated with silica, and unidirectional solidification was carried out at the rate of 1 mm/min. Cutting removal of the ingot upper part was carried out after coagulation. The impurity analysis value of the obtained ingot is shown in Table 5.

[0040]

[Table 5]

シリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
シリコン原料粉	0.3	0.3	250	100	20	実施例
シリコンインゴット	0.2	0.1	< 1	< 5	<5	実施例

[0041]

[Effect of the Invention]By this invention, sludge of the semiconductor silicon thrown away conventionally can use it as a raw material for solar cells, it is stabilized and a raw material required for a solar cell can be secured now.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention]Especially this invention relates to the manufacturing method of the high purity silicon which can be used as a raw material of the silicon for solar cells about manufacture of high purity silicon.

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PRIOR ART

[Description of the Prior Art]In recent years, from the demand of diversification of an energy source, photovoltaics is brought into the limelight and research and development are briskly done towards utilization of a low-price power plant. In such a situation, as a raw material for solar cells, silicon is a material which is the easiest to be used widely, and, moreover, importance is most attached to it as a material used for the electric power supply for power.
[0003]The silicon which can serve as a raw material of a solar cell is purity. It is not less than 99.9999%, and is specific resistance. A high grade called 0.5-10-ohmcm (it converts into B concentration in silicon, and is 0.2 ppm or less) is demanded.
The substandard article by which it is generated when the high purity silicon used by semiconductor industry or the substrate for IC is manufactured conventionally is used.
However, the high purity silicon for semiconductors is expensive, and there are few yields of a substandard article, and quantity has a limitation. From now on, the increase in a solar cell is expected and reservation of the silicon source for solar cells has been important SUBJECT.
[0004]Since it is such, the method which is moreover stabilized and can supply the silicon for solar cells cheaply is examined, and many proposals are made. For example, as a method of manufacturing the above-mentioned high purity silicon from commercial silicon (purity 99.5wt%), About metallic impurity elements, such as aluminum, Fe, and Ti, unidirectional solidification refining using a solid-liquid distribution coefficient being small removes, and about C. When it is SiC, deposit the surface in the case of coagulation, and when dissolving, it removes as CO, On the other hand about P, decompression removal is carried out using steam pressure being high, and the method of removing by Ar plasma dissolution which added H_2O, CO_2, or O_2 is proposed about B.
[0005]However, in the above-mentioned manufacturing method, the removing methods of each impurity element differed, respectively, and there were problems, such as a fall of the yield by the loss at the time of a process shifting not only to becoming complicated but to a next process. On the other hand, P in the metal silicon of marketing by these days and electron beam melting, Ca, It is reported that simultaneous removal of aluminum, C, and B is possible (ISIJ Intrernational, Vol.32 (1992), No.5, P.635 to P.642), and simplification of the manufacturing process is expected. However, this is a thing of the grade that B

concentration in silicon decreased to about 10 ppm.
Below B concentration made into the target as solar cell silicon is not reached.

[0006]On the other hand, although the way unidirectional solidification refining using electron beam melting removes an impurity is proposed by JP,H5-124809,B, Unidirectional solidification refining was difficult for the mechanisms of refining performing efficient removal of B etc. which are impurities with the solid-liquid distribution coefficient near 1 unlike refining by evaporation. For example, blow powdered silica into molten-metal silicon, JP,5-31488,B is made to generate SiO gas, and the method of making high purity silicon profitably like is proposed by returning to metal Si within the layer with which the reducing agent filled up ** SiO gas.
[0007]The silicon for metallurgy is fused as a starting material, while flying an arc to inter-electrode [which was provided in melted silicon and the upper part], to JP,H5-246706,A, it refines inactive gas and by adding a oxidizing gas preferably, and the method of obtaining high purity silicon is proposed. However, it is difficult to remove B and P in silicon, the actual condition is have not shifted to industrial production, and the problem that it is stabilized cheaply and the source of high purity silicon for obtaining a high-purity-silicon board cannot be secured is left behind.

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EFFECT OF THE INVENTION

[Effect of the Invention]By this invention, sludge of the semiconductor silicon thrown away conventionally can use it as a raw material for solar cells, it is stabilized and a raw material required for a solar cell can be secured now.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]This invention solves an aforementioned problem advantageously and an object of this invention is to propose the manufacturing method of the silicon ingot which can obtain the high purity silicon for solar cells using the silicon precursor powder used as the raw material of the high purity silicon for solar cells or a pellet, these precursor powder, and a pellet.

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MEANS

[Means for Solving the Problem]This invention persons constituted this invention, as a result of examining a utilizing method of sludge wholeheartedly as a silicon source paying attention to silicon sludge discarded conventionally. Namely, this invention is made from silicon sludge which uses as the main ingredients silicon by which it is generated when slicing a silicon ingot and processing it into a silicon wafer, An acid-dipping process of this solid content being immersed in an acid solution, and removing an impurity after separating solid content from this raw material, A physical separation process of being a manufacturing method of silicon precursor powder for solar cells passing through washing and a drying process furthermore, and removing an impurity from this solid content by a physical means after separating solid content from silicon sludge, Subsequently, they are an acid-dipping process and a manufacturing method of silicon precursor powder for solar cells which passes through washing and a drying process further. Even if a magnetic-separation process which passes inside of a magnetic field beyond 1T is used for this invention as a process of removing an impurity from this solid content, subsequently an acid-dipping process may be used for it with a magnetic-separation process which passes inside of a magnetic field beyond 1T. It is good also as a two-step magnetic-separation process that said magnetic-separation process passes inside of a magnetic field beyond 1T in this invention after passing inside of a magnetic field below 1T, or a magnetic field beyond 1T for this solid content, and, as for formation of a magnetic field more than said 1T, it is desirable to use a superconductivity magnet. Silicon precursor powder manufactured by a method which this invention described above. Or it is a manufacturing method of a silicon ingot for solar cells considering it as an ingot according to a melting process which supplies a silicon material pellet which hardened this silicon precursor powder to a fused high-purity-silicon bath, and is dissolved, and a coagulating process which solidifies melted silicon by unidirectional solidification. Said melting process of this invention is good also as a melting process which blows all of this silicon precursor powder, or one copy into a melting high-purity-silicon bath with inactive gas or hydrogen gas.
[0010]
[Embodiment of the Invention]In this invention, silicon sludge is used as a raw material. Silicon sludge is generated, when slicing a silicon ingot and processing it into a silicon wafer. On the occasion of this slice,

tens of% of silicon serves as cutting waste by end cost. Since impurities increased in number, the sludge generated at this time was discarded conventionally [all]. The high-purity-silicon powder by which it is generated in it when cutting an ingot in this sludge, and the alumina by which it is generated by wear of the edge of a cutting machine, etc. at the time of cutting, Impurities, such as corundum, iron oxide, iron hydroxide, silica, barium oxide, magnesium oxide, Cu, and C, mix physically, and serve as slurry form.

[0011]Silicon sludge removes the cutting oil first contained in a slurry, and separates solid content, such as silicon powder. Silicon sludge may grind if needed. When the viscosity of a slurry is low, it is preferred to apply and separate into the filter press or a centrifuge. When the viscosity of a slurry is high, since the fluid which can serve as a solvent of cutting oil, such as warm water, is added to a slurry and viscosity is reduced, it is desirable to perform the same separation as the above. When removal of cutting oil is insufficient, it is good to melt again the solid content produced by dissociating at the time of a solvent, to consider it as slurry form, and to repeat separation.

[0012]The cutting oil of a silicon ingot has the desirable cutting oil of water solubility [lessen / environmental problems, such as making the above-mentioned separation work easy or effluent processing,]. Next, an impurity is separated from solid content. As one of the separation methods, an acid-dipping process is taken by this invention. Using an acid solution, solid content is supplied in an acid solution and an impurity is removed. A metal impurity especially Cu, and Fe are removed by processing by this acid solution. A hydrochloric acid aqueous solution or the mixed water solution of chloride and nitric acid is preferred for the acid used here. Especially the concentration of solution has a 5-20 vol% hydrochloric acid aqueous solution and a preferred 5-20 vol% chloride+1-10vol% nitric acid mixed water solution.

[0013]A physical means may be used and an impurity may be removed. Especially as a physical means, although not limited, in especially this invention, particle classification, flotation, and magnetic separation are preferred. These may be applied independently or it may apply combining these. A physical means and acid dipping may be combined. It is the way the specific gravity or weight separates particles, a sedimentation method and a centrifuge method are preferred for a particle classification also in the method of separating by a wet type especially in this invention, and a clear decollator (clarifier) and precipitate concentration device (thickener) or the separator of a centrifugal type is preferred for it.

[0014]Thereby, refractories, the coarse-grain impurity from a cutting tool, carbon, copper, and SiC are mainly disengageable among impurities. Flotation is the way control the wetting of a solid surface using the adsorption in solution, and air bubbles separate particles. The pH of a solution is controlled, or a collector is added and it dissociates further using a depressant and an active agent. Thereby, carbon and SiC can mainly dissociate.

[0015]It is going to separate magnetic separation within an uneven magnetic field using the difference of the magnetism of particles. Generally, when a dispersoid and carrier fluid exist, it is relative magnetization M^*. [0016]

[Equation 1]

$$M^{-1}=\frac{9\ (\chi_p-\chi_f)}{(3+\chi_p)\ (3+\chi_f)}H$$

[0017]here -- chi_p: -- bulk susceptibility chi_f: of a dispersoid -- bulk susceptibility H of carrier fluid : What is shown by magnetic field strength is known well. Also in space with magnetization inclination, the magnetic force proportional to relative magnetic susceptibility and inclination generates the mixed particles, and the power can separate. The magnetic force of the size of $F^{**}M^{*}{}^{**}H$ occurs. If even one step of magnetic separations are used together with other separation methods, high-purity-silicon precursor powder can be obtained. However, by the substance of feeble magnetism, an upper type is approximated by $M^{*}=(chi_p - chi_f)$ H. For example, underwater chi_p of Al_2O_3 has only an order of 10^{-5}, and is small double figures as compared with chi_p (order of 10^{-3}) of ferromagnetic substance Fe_2O_3. The separation between them was impossible for other feeble magnetism substance chi_p to the 10^{-5} order.

[0018]Since magnetizing force cannot overcome Brownian motion in the case of particles especially with small particle diameter, separation is difficult. Then, after performing magnetic separation which have a magnetic field below 1T, or a magnetic field beyond 1T in this invention and separating a ferromagnetic impurity, it is preferred to apply magnetic separation which have a magnetic field beyond 1T. In one step of magnetic separations, it is because a substance of feeble magnetism, such as Al_2O_3, is inseparable.

[0019]This becomes separable [alumina and a phosphorylation thing]. A magnetic field is formed in magnetic separation which have a magnetic field beyond 1T still more preferably using a superconductivity magnet. Pour a fluid to be dissociated in a strong magnetic field formed during magnetization of a super-conductive magnet, very small particles are made to adhere to a filament according to electromagnetic force, and separation of feeble magnetism particles is enabled.

[0020]By the above-mentioned process, after removing an impurity in solid content, it is considered as silicon precursor powder through a drying process which is washed further with water and dried. Silicon precursor powder after drying is usually fines of 50 micrometers or less (-320 meshes). This silicon precursor powder has not less than 99.99% of purity. Although a granular material may still be sufficient as silicon precursor powder, it is good also as a silicon material pellet which was corned and was made into a pellet type.

[0021]Drawing 1 is process drawing showing one example of a manufacturing process of silicon precursor powder. Thus, manufactured silicon precursor powder or a silicon material pellet is supplied to a high-purity-silicon bath fused beforehand, unidirectional solidification is dissolved and carried out to it, and an ingot is manufactured. As for the dissolution, it is preferred under inert atmospheres, such as Ar, to carry out in a silica crucible.

[0022]although it may carry out in an inert gas atmosphere when throwing silicon precursor powder into a silicon bath -- Ar or H_2 -- the -- if a part is all blown during a silicon bath, carbon in silicon is removable by oxygen of an oxide film on the surface of precursor powder. Since an impurity with insufficient removal and an impurity mixed from refractories etc. in a melting process are contained in fused silicon, silicon after melting is solidified with an unidirectional solidification process, an impurity is brought together in a

last solidified part, and cutting removal is carried out after solidifying this. Two or less mm/min is desirably suitable for coagulation speed in unidirectional solidification at this time 5 or less mm/min.
[0023]When purity of melted silicon is low, for reduction of B, Ar plasma dissolution which added H_2O, CO_2, and O_2 can remove further, for example. To in that case, inside of plasma gas It is preferred to add H_2O not more than 10vol%, CO_2, and O_2. A manufacturing process of a silicon ingot is shown in drawing 2.

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EXAMPLE

[Example]
[Working example 1] The silicon sludge (solid content) which centrifuges silicon sludge when the monocrystal substrate for semiconductors is sliced after a crack in warm water, separates cutting oil, and is shown in Table 1 was obtained. After 5 kg of the above-mentioned solid content is immersed in the mixed acid aqueous solution 5l containing HCl 10vol %+$HNO_3$5 vol%, it is rinsed, and it dries, and is silicon precursor powder. 4.5 kg was obtained. The concentration of the impurity of this silicon precursor powder is shown in Table 1.
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It cast to the graphite mold which coated this with silica, and heated from the upper part, and unidirectional solidification was carried out at the rate of 1 mm/min by cooling from the lower part.
After coagulation, cutting removal of 15% of the upper part of an ingot was carried out, and 6.1kg silicon was obtained. The purity of the obtained silicon ingot is shown in Table 1. It is purity sufficient as silicon for solar cells, and about 70% of silicon sludge (solid content) is able to use as silicon for solar cells.
[0026]What supplied to the high-purity-silicon bath, dissolved, separates liquid from sludge and used [unidirectional solidification only of the dry solid content was carried out, and] it as the ingot was made into the comparative example. A comparative example has many impurities, such as C, Fe, and Cu.
[0027]
[Table 1]

シリコン原料粉およびシリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
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シリコン原料粉	0.4	0.1	500	300	4000	実施例
シリコンインゴット	0.3	<0.1	10	15	45 *	実施例
シリコンインゴット	0.5	0.3	100	35	80 *	比較例

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[0028][Working example 2] Silicon precursor powder obtained like working example 1 After supplying 5.0 kg on the bath surface of the high purity silica (3 kg) for semiconductors dissolved by the silica crucible heated at 1500 ** in Ar atmosphere and dissolving, Furthermore, the silicon precursor powder 500g was blown into melted silicon with Ar gas using the silica tube. Melted silicon obtained since the splash occurred by gas blowing in at this time It was 7.1 kg. It cast to the graphite mold which coated this with silica, and heated from the upper part, and unidirectional solidification was carried out at the rate of 1 mm/min by cooling from the lower part. After coagulation, cutting removal of 15% of the upper part of an ingot was carried out, and a 6-kg silicon ingot was obtained. The obtained silicon ingot impurity analysis value is shown in Table 2. The carbon content in the silicon ingot obtained eventually was set to 5 ppm or less. It has purity sufficient as silicon for solar cells. The quantity of the silicon obtained eventually is equivalent to 60% of silicon precursor powder.

[0029]

[Table 2]

シリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
シリコンインゴット	0.15	<0.1	10	15	<5.0	実施例

[0030][Working example 3] Silicon sludge when the monocrystal substrate for semiconductors was sliced was immersed in warm water, the centrifuge separated the fluid, and the silicon sludge (solid content) of the same purity as the purity shown in Table 1 was obtained. After giving the magnetic separation of the 2nd step in the magnetic field which generated the above-mentioned silicon sludge (solid content) with the superconductivity magnet of 3T after giving magnetic separation in the magnetic field of 0.8T, it rinsed and dried and silicon precursor powder was obtained. The impurity analysis value of this silicon precursor powder is shown in Table 3.

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[0032]The impurity analysis value of the obtained ingot is shown in Table 3. Removal reduction is fully

carried out and the impurity has purity sufficient as silicon for solar cells.
[0033]
[Table 3]
シリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
シリコン原料粉	0.3	0.2	100	50	15	実施例
シリコンインゴット	0.2	<0.1	< 1	<5	<5	実施例

[0034][Working example 4] Silicon sludge when the monocrystal substrate for semiconductors was sliced was immersed in warm water, the centrifuge separated the fluid, and the silicon sludge (solid content) of the same purity as the purity shown in Table 1 was obtained. After giving the magnetic separation of the 2nd step in the magnetic field which generated the above-mentioned solid content with the superconductivity magnet of 3T after giving magnetic separation in the magnetic field of 1.5T, it was immersed into a 20% hydrochloric acid aqueous solution, and the impurity was removed. Then, after removing an acid solution, it rinsed and dried and silicon precursor powder was obtained. The impurity analysis value of this silicon precursor powder is shown in Table 4.
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シリコン原料粉	0.2	0.1	30	15	<5	実施例
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[0038][Working example 5] After silicon sludge when the monocrystal substrate for semiconductors was sliced was immersed in warm water, it was considered as silicon sludge (solid content) with the centrifuge. This solid content was immersed into 20 more%HCl solution, after giving magnetic separation in the magnetic field of 1.5T, and the impurity was removed. Then, after removing an acid solution, it rinsed and dried and silicon precursor powder was obtained. The impurity analysis value of this silicon precursor powder is shown in Table 5.
[0039]Next, the silicon ingot was manufactured using the obtained silicon precursor powder. Silicon precursor powder was thrown in on the bath surface of the high purity silicon for semiconductors which

dissolved by the silica crucible, and it dissolved. Melted silicon was cast to the graphite mold coated with silica, and unidirectional solidification was carried out at the rate of 1 mm/min. Cutting removal of the ingot upper part was carried out after coagulation. The impurity analysis value of the obtained ingot is shown in Table 5.

[0040]

[Table 5]

シリコンインゴットの不純物分析値（ppmw）

	B	P	Fe	Cu	C	備考
シリコン原料粉	0.3	0.3	250	100	20	実施例
シリコンインゴット	0.2	0.1	< 1	< 5	<5	実施例

[Translation done.]

* NOTICES *

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damages caused by the use of this translation.**

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is process drawing showing an example of a process which manufactures the silicon precursor powder of this invention.
[Drawing 2]It is process drawing showing an example of a process which manufactures the silicon ingot of this invention.

[Translation done.]

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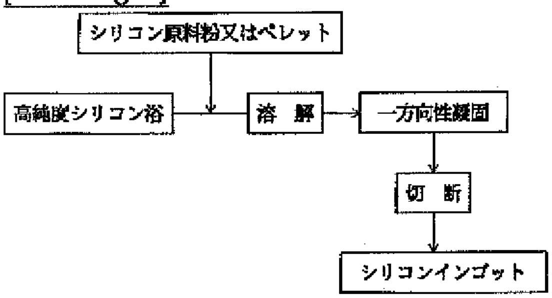
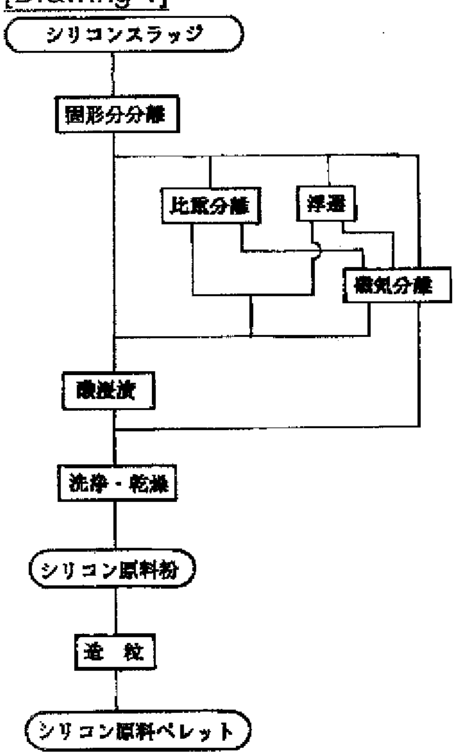
DRAWINGS

[Drawing 2]



[Drawing 1]



[Translation done.]